PATENT SPECIFICATION

(11) 1 572 900

(21) Application No. 1546/79 (22) Filed 21 April 1976
(62) Divided out of No. 1572898
(23) Complete Specification filed 19 April 1977
(44) Complete Specification published 6 Aug. 1980
(51) INT CL³ F25J 1/02//3/02
(52) Index at acceptance
F4P 723 732 CA

(19)

1 572 900

(72) Inventors PETRUS FRANCISCUS ANTONIUS VAN GRINSVEN and MAARTEN JAMES PIKAAR

(54) A PROCESS FOR THE LIQUEFACTION OF NATURAL GAS

(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a method of liquefying a natural gas by cooling it under pressure in stages, comprising passing a natural gas stream in heat-exchange relationship with a mixed refrigerant circulating in a circuit.

This patent application and the copending patent application 1545/79 (Serial No. 1572899) are divisional patent applications of copending patent application 16112/76 (Serial No. 1572898).

It is an object of the invention to use at least one mixed refrigerant to produce a cooling effect by allowing said mixed refrigerant to evaporate only partly.

According to the present invention there is provided a method of liquefying a natural gas by cooling it under pressure in stages, comprising passing a natural gas stream in heat-exchange relationship with a first mixed refrigerant circulating in a first circuit and successively passing the natural gas stream in heat-exchange relationship with at least a second mixed refrigerant circulating in a second circuit, wherein the said refrigerants are of different compositions, raising the pressure of the first mixed refrigerant in a compressor installation; cooling the compressed first refrigerant so that it condenses partially; separating the liquid fraction from the gaseous fraction in a first separator; cooling the liquid fraction further; reducing the pressure of the liquid fraction in an expansion device and causing the expanded liquid fraction to evaporate partly to produce a cooling effect which cooling effect is used for cooling the natural gas stream, for cooling the said separated liquid fraction before it is expanded, and for cooling the said separated gaseous fraction.

The method according to the invention comprises preferably further, cooling at least part of the said separated gaseous fraction to such a degree that it liquefies; reducing its pressure in an expansion device and causing it to evaporate partly to produce a cooling effect for the said purposes.

In an attractive embodiment of the method according to the invention, the said cooling effect is also used for cooling the second refrigerant after the pressure of the latter has been raised in a compressor.

Before the liquefaction of the natural gas, it is necessary to remove water from the natural gas. In a possible embodiment of the method according to the invention, the water is removed from the natural gas by precooling it. This embodiment of the invention comprises branching off part of the liquid fraction after its removal from the first separator; reducing the pressure of the branched-off part in an expansion device and allowing it to evaporate to precool natural gas in order to remove water from the natural gas.

Further details and embodiments of the process according to the invention will be explained with reference to the drawing, accompanying the Provisional Specification showing a flow sheet of the process.

Referring to the drawing, natural gas, from which CO_2 and water have been removed, is supplied through a line 1.

This natural gas, which is at a relatively high pressure of, for example, 50 bar and at a temperature of, for example, 20 degrees centigrade, is passed through a coil 2 of a heat-exchanger 4. In the coil 2 the temperature of the natural gas is lowered. The cooled natural gas leaving the coil 2 is passed through a line 3 to a phase separator 5, wherein condensed heavier hydrocarbon

components are separated from the gas. The condensed heavier hydrocarbons are removed from the phase separator 5 through a discharge line 6. Together with the condensate some lighter hydrocarbons, such as methane, ethane and propane are removed from the separator 5 through the discharge line 6. The natural gas leaves the phase separator 5 as a vapour and is passed through a line 7 to a coil 8 of the heat-exchanger 4, wherein the temperature of the natural gas is lowered further. From coil 8 the cooled natural gas, which contains a small quantity of liquid, is passed through a line 9 to a coil 10 of a heat-exchanger 11. In coil 10 the temperature of the natural gas is reduced to a lower value, so that more liquid is formed. From coil 10 the natural gas is passed through a line 12 to a phase separator 13. In phase separator 13 condensed hydrocarbons are separated from the natural gas. The condensed hydrocarbons, which contain, for example, mainly methane, ethane, propane and butane as well as some pentane, are removed from the separator 13 through a line 14.

Natural gas vapour containing mainly methane, ethane and nitrogen leaving the phase separator 13 is passed through a line 15 to a coil 16 of heat-exchanger 11, wherein the temperature of the natural gas is lowered further and the natural gas is fully condensed. From coil 16 the natural gas is passed to an expansion device 17. In expansion device 17 the pressure of the condensed natural gas is reduced, whereafter it is passed via a line 18 to a coil 19 of heat-exchanger 11.

In coil 19 the condensed natural gas is cooled further to a temperature of, for example, minus 147 degrees centigrade. From coil 19 the liquefied natural gas is passed through a line 20 to a heat-exchanger 22 in a nitrogen stripper 21. In the heat-exchanger 22 the liquefied natural gas is cooled further. From heat-exchanger 22 the liquefied natural gas is passed to an expansion device 23. In expansion device 23 the liquefied natural gas is expanded to a lower pressure, so that some vapour is formed, and then it is passed through a line 24 to a distribution device 25 in the stripper 21, wherein liquid and vapour are separated. The liquid natural gas fraction leaving distribution device 25, passes through the stripper 21 to an outlet 26 and from outlet 26 via line 27 to storage. In stripper 21 nitrogen is separated from the liquefied natural gas. A methane/nitrogen vapour mixture containing some traces of ethane leaves the top of the stripper 21 via a line 29 and is passed to a heat-exchanger 30. In heat-exchanger 30 the temperature of this gas mixture is raised and then this gas mixture is passed through a line 31 to a heat-exchanger 32 in which the temperature of the said gas mixture is raised further. Finally, the said gas mixture is passed from heat-exchanger 32 through a line 33 to a suitable location to be used, for example, as a fuel gas.

The condensate leaving the phase separator 5 is passed via line 6 and an expansion device 150 to a demethanizer 151 which is provided with a reboiler 152. A heavy hydrocarbon stream, comprising ethane and components heavier than ethane is removed as liquid from the bottom of the demethanizer 151 and is passed to a refrigerant make-up unit (not shown) via a line 153. In the refrigerant make-up unit hydrocarbons may be produced which are selected from the group comprising C_2-, C_3-, C_4- and C_5- hydrocarbons. Part of the liquid leaving the demethanizer 151 through line 153 is recirculated through the reboiler 152. Methane, possibly with some ethane, leaves the demethanizer 151 as overhead vapour and is passed through a line 154 to be intermixed with a gas stream flowing in a line 157.

The C_2-hydrocarbons produced in the refrigerant make-up unit are passed via a line 141 to the heat-exchanger 32 to be lowered in temperature. From heat-exchanger 32 the said C_2-hydrocarbons are passed via a line 142 to storage. The C_3-hydrocarbons produced in the refrigerant make-up unit are passed via a line 143 to the heat-exchanger 32. In heat-exchanger 32 the said C_3-hydrocarbons are lowered in temperature and then passed via a line 144 to storage.

The condensed hydrocarbons leaving the phase separator 13 via line 14 can be passed via a line 158 to an expansion device 159. Another part of said condensed hydrocarbons can be passed via a pump 160 to the gas flowing in line 15 to be intermixed therewith.

In expansion device 159 the liquid is expanded to a lower pressure and then it is passed to a de-methanizer 162 which is provided with a reboiler 163. A hydrocarbon steam comprising mainly ethane, propane and butane is removed as liquid from the bottom of the demethanizer 162 and is passed as raw natural gas liquid via a line 164 to storage for further treatment. Part of the liquid leaving the demethanizer 162 through line 164 is recirculated through the reboiler 163. Methane, possibly with some ethane, leaves the demethanizer 162 as overhead vapour and is passed via the line 157 to a coil 165 in heat-exchanger 11. In coil 165 the gas is cooled and condensed and then it is passed via a line 166 to the gas flowing in line 18 to be intermixed therewith.

The quantity of liquid to be passed to the

demethanizer 162 can be controlled at will by manipulating the expansion device 159. In so doing the extraction of natural gas liquids from the natural gas feed stream can be regulated. All condensate from separator 13 which is not sent to demethanizer 162 is passed via pump 160 to line 15.

In the above natural gas liquefaction system two separate cooling circuits are used. In the first cooling circuit a so-called mixed refrigerant (a first mixed refrigerant), for example a suitable mixture of methane, ethane, propane, butane and pentane, is supplied in gaseous condition through a line 34 to a compressor 35. In compressor 35 the pressure of the first mixed refrigerant is raised. From compressor 35 the first mixed refrigerant is passed through a line 36 to a heat-exchanger 37, which is cooled for example by water. In heat-exchanger 37 the first mixed refrigerant is cooled to such a degree that partial condensation of the mixture occurs. From heat-exchanger 37 the partially condensed first mixed refrigerant is passed through a line 38 to a phase separator 39 in which condensed first mixed refrigerant is separated from gaseous first mixed refrigerant. The gaseous first mixed refrigerant is passed from phase separator 39 through line 40 to a compressor 41. In compressor 41 the pressure of the gaseous first mixed refrigerant is raised further. From compressor 41 said gaseous first mixed refrigerant is passed through a line 42 to a heat-exchanger 43.

The condensed first mixed refrigerant leaves the phase separator 39 via outlet 44 and is passed to a pump 45. In pump 45 the pressure of the condensed first mixed refrigerant is raised to such a level that it can be passedd through a line 46 to line 42 and be added to the gaseous first mixed refrigerant leaving the compressor 41. In the heat-exchanger 43, which is, for example, cooled by water, the first mixed refrigerant is cooled and partially condensed and from heat-exchanger 43 the cooled first mixed refrigerant is passed through a line 47 to a first phase separator 48.

The condensed first mixed refrigerant leaving the phase separator 48 is passed through a line 49 to a coil 50 of the heat-exchanger 4. The gaseous first mixed refrigerant leaving the phase separator 48 is passed through a line 51 to a coil 52 of the heat-exchanger 4.

In coil 50 the condensed first mixed refrigerant is cooled and is then passed from coil 50 via a line 53 to an expansion device 54. In expansion device 54 the cooled liquid first mixed refrigerant is expanded to a lower pressure. The liquid, possibly together with a small portion of vapour, is passed from expansion device 54 through a line 55 and is injected through a distribution device 56 into heat-exchanger 4, wherein it combines with a first mixed refrigerant stream which enters heat-exchanger 4 via a distribution device 64. The combined first mixed refrigerant stream flows downward over the coils 50, 52, 100 and 2 to cool the contents of these coils. During this process the largest part of the first mixed refrigerant evaporates. The first mixed refrigerant, which is largely in gaseous condition and contains only a small portion of liquid, leaves the heat-exchanger 4 via a line 57 to be passed to a second phase separator 58. In phase separator 58 liquid first mixed refrigerant is separated from gaseous first mixed refrigerant. The separated liquid first mixed refrigerant is removed from phase separator 58 via an outlet 76 to be injected, after its pressure has been raised, into, for example, line 36, or into, for example, separator 39. Via a line 59 so-called "make-up refrigerant" is added to the first refrigerant passing through line 57 to compensate for first refrigerant lost during the process. Gaseous first refrigerant is passed from phase separator 58 via line 34 to compressor 35 to repeat the cycle as described in the above.

The first mixed refrigerant passing through coil 52 is lowered in temperature and condensed in said coil and is then passed to a further coil 60 of heat-exchanger 4.

In coil 60 the condensed first mixed refrigerant is cooled further and then it is passed via a line 61 to an expansion device 62. In expansion device 62, the first refrigerant is expanded to a lower pressure so that some vapour is formed and then it is passed via a line 63 to a distribution device 64. From distribution device 64 the first refrigerant, which is largely in liquid condition, flows downward over the coils 60, 101 and 8 to cool the contents of these coils and further downward over the coils 50, 52, 100 and 2 to cool the contents of these coils until it reaches the bottom of the heat-exchanger.

During this process the first refrigerant evaporates largely. Finally, the first refrigerant leaves the heat-exchanger 4 via the line 57 to be passed to phase separator 58.

Some of the condensed first refrigerant leaving the phase separator 48 via the line 49 is branched off and is passed through a line 65 to an expansion device 66. In expansion device 66 the first refrigerant is expanded to a lower pressure so that some gas is formed and is then passed through a line 67 to a distribution device 68 of a heat-exchanger 69 which is provided with a coil 70. The first refrigerant, which is largely in liquid condition, leaving the distribution device 68

flows downward over the coil 70 to cool the contents of the coil 70. During this process the first refrigerant evaporates largely and finally leaves the heat-exchanger 69 through a line 71.

Via line 71 the first refrigerant is passed to an expansion device 72 in which the first refrigerant is expanded to a lower pressure. Then the first refrigerant, which is largely in gaseous condition, is passed from the expansion device 72 to the phase separator 39 via a line 73 to be combined with the first refrigerant arriving from the compressor 35. In heat-exchanger 69 natural gas to be liquefied is precooled in order to remove a quantity of water which is present in the natural gas. For this purpose the natural gas is supplied through a line 74 to the coil 70 and passed through coil 70. The natural gas precooled in coil 70, leaves the coil 70 via a line 75 and is passed to a phase separator (not shown) in which condensed water is removed from the natural gas. Then the partly dried natural gas is passed to a conventional drier (not shown) to remove the remaining water from the natural gas. This conventional drier is, for example, of the kind containing a suitable desiccant. From the conventional drier the natural gas is passed to line 1 in order to be liquefied in the manner as described in the above.

In the second cooling circuit a so-called mixed refrigerant (a second mixed refrigerant) is circulating as well. The composition of the second mixed refrigerant circulating in the second cooling circuit is, however, different from the first mixed refrigerant circulating in the first cooling circuit. The second mixed refrigerant circulating in the second cooling circuit is, for example, a mixture of ethane, methane and nitrogen.

In the second cooling circuit gaseous second mixed refrigerant is supplied through a line 80 to a compressor 81.

In the compressor 81 the pressure of the second mixed refrigerant is raised and then it is passed through a line 82 to a heat-exchanger 83, which is cooled, for example, by water. In heat-exchanger 83 the second mixed refrigerant is cooled and then it is passed via a line 84 to a knock-out vessel 85 in which liquid components, if any, can be removed in conventional manner. From knock-out vessel 85 the second mixed refrigerant is passed via a line 86 to a compressor 87.

In compressor 87 the pressure of the second mixed refrigerant is raised further and then it is passed via a line 88 to a heat-exchanger 89 which is cooled, for example, by water. From heat-exchanger 89, the second mixed refrigerant is passed via a line 90 to a coil 100 of the heat-exchanger 4. In coil 100 the temperature of the second mixed refrigerant is lowered. From coil 100, the second mixed refrigerant is passed to a coil 101 in which it is cooled further and partially condensed.

From coil 101 the cooled second mixed refrigerant is passed through a line 102 to a phase separator 106. In the phase separator 106 the gaseous second refrigerant is separated from liquid second refrigerant. From phase separator 106, the liquid second refrigerant is passed through a line 110 to a coil 111 of the heat-exchanger 11. In coil 111 the second refrigerant is cooled further and then it is passed through a line 112 to an expansion device 113. In expansion device 113 the second refrigerant is expanded, whereafter it is passed through a line 114 and is injected through a distribution device 115 into the heat-exchanger 11, wherein it combines with a second mixed refrigerant stream which enters heat-exchanger 11 via a distribution device 132.

The combined second mixed refrigerant stream is passed over the coils 111, 127, 165, 16 and 10 which causes cooling of the contents of these coils. During the passage of the second refrigerant over the coils 111, 127, 165, 16 and 10 the second refrigerant evaporates at least partly.

Finally, the second refrigerant reaches the lower part of the heat-exchanger 11 and then it is passed through a line 116 to a heat-exchanger 117.

In heat-exchanger 117, the second refrigerant cools the contents of a coil 109 of the heat-exchanger 117. Then the second refrigerant is passed through a line 118 to a knock-out vessel 119. Finally, the second refrigerant, which is in gaseous condition, is passed from knock-out vessel 119 through the line 80 to the compressor 81 to repeat the cycle.

Gaseous second refrigerant leaves the phase separator 106 through a line 125. From line 125 part of the said gaseous second refrigerant is passed through a line 126 to a coil 127 in the heat-exchanger 11 in which it is cooled and condensed. From coil 127 the condensed second refrigerant is passed to a coil 128 in which it is cooled further. From coil 128 the second refrigerant is passed via a line 129 to an expansion device 130 in which the second refrigerant is expanded to a lower pressure. From expansion device 130, the second refrigerant, which is now largely in liquid condition is passed via a line 131 to a distribution device 132. From distribution device 132, the second refrigerant is passed downward over the coils 19, 128, 16, 165, 10, 127 and 111 to the bottom part of the heat-exchanger 11. During the passage of the second refrigerant, the latter cools the contents of the said coils.

Finally, the second refrigerant leaves the heat-exchanger 11 through the line 116.

Part of the gaseous second refrigerant leaving the phase separator 106 via the line 125 is branched off and is passed via a line 135 to the heat-exchanger 30. In heat-exchanger 30 the second refrigerant is cooled against gaseous mixture leaving the nitrogen stripper via the line 29. From heat-exchanger 30 the second refrigerant is passed via a line 136 to an expansion device 137.

In expansion device 137 the second refrigerant is expanded to the pressure of the second refrigerant leaving the expansion device 130. Finally, both streams of second refrigerant are mixed and led via line 131 to the distribution device 132 to be injected into the heat exchanger 11.

Part of the second mixed refrigerant passing through line 90 is recycled. For this purpose, part of the gas stream is branched off and is passed via a line 138 to the coil 109 of the heat-exchanger 117. In coil 109 the temperature of the second mixed refrigerant is lowered and then it is passed from coil 109 through a line 139 to line 102 to be intermixed with the second mixed refrigerant passing through line 102 to be passed to the phase separator 106.

At 120 make-up refrigerant is added to the second refrigerant circuit to compensate for losses of refrigerant circulating in the circuit.

WHAT WE CLAIM IS:—

1. A method of liquefying a natural gas by cooling it under pressure in stages, comprising passing a natural gas stream in heat-exchanger relationship with a first mixed refrigerant circulating in a first circuit and successively passing the natural gas stream in heat-exchanger relationship with at least a second mixed refrigerant circulating in a second circuit, wherein the said refrigerants are of different compositions, raising the pressure of the first mixed refrigerant in a compressor installation; cooling the compressed first refrigerant so that it condenses partially; separating the liquid fraction from the gaseous fraction in a first separator; cooling the liquid fraction further; reducing the pressure of the liquid fraction in an expansion device and causing the expanded liquid fraction to evaporate partly to produce a cooling effect, which cooling effect is used for cooling the natural gas stream, for cooling the said separated liquid fraction before it is expanded, and for cooling the said separated gaseous fraction.

2. The method as claimed in claim 1, comprising cooling at least part of the said separated gaseous fraction to such a degree that it liquefies; reducing its pressure in an expansion device and causing it to evaporate partly to produce a cooling effect for the said purposes.

3. The method as claimed in any one of the claims 1—2, wherein said cooling effect is also used for cooling the second refrigerant after the pressure of the latter has been raised in a compressor.

4. The method as claimed in any one of claims 1—3, comprising collecting the gas/liquid mixture resulting from the expanded and thus partly evaporated liquid first refrigerant; passing said gas/liquid mixture to a second separator; separating liquid refrigerant from gaseous refrigerant; passing the gaseous refrigerant to a compressor for raising its pressure, and causing it to repeat the cycle.

5. The method as claimed in claim 4, comprising removing the separated liquid refrigerant from said second separator; raising its pressure and injecting it into the stream of the gaseous refrigerant from said separator after the pressure of the latter has been raised in the compressor.

6. The method as claimed in any one of claims 1—5, comprising branching off part of the liquid fraction after its removal from the first separator; reducing the pressure of the branched-off part in an expansion device and allowing it to evaporate to precool natural gas in order to remove water from the natural gas.

7. The method as claimed in claim 6, wherein the said branched-off part of the liquid fraction of the refrigerant after its evaporation is injected into the stream of gaseous refrigerant after the pressure of the latter has been raised in a compressor.

8. The method as claimed in any one of claims 1—7, comprising raising the pressure of the second refrigerant in a compressor installation; cooling the second refrigerant so that a liquid and a gaseous fraction is formed; separating the liquid fraction from the gaseous fraction in a separator; cooling the separated liquid fraction; reducing the pressure of the cooled liquid fraction in an expansion device and causing the expanded liquid fraction to evaporate at least partly for cooling the natural gas stream, for cooling the said separated liquid fraction of the second refrigerant before it is expanded, and for cooling at least part of the separated gaseous fraction of the second refrigerant.

9. The method as claimed in claim 8, comprising cooling at least part of the said gaseous fraction of the second refrigerant separated in the separator from the liquid fraction of the second refrigerant to such a degree that it condenses, after said condensation further cooling the said condensed second refrigerant, reducing its pressure in an expansion device and causing it to evaporate at least partly for cooling the

natural gas, for cooling the said separated liquid fraction of the second refrigerant before it is expanded and for cooling at least part of the separated gaseous fraction of the second refrigerant.

10. The method as claimed in claim 9, wherein part of the gaseous fraction of the second refrigerant, after separation in the separator from the liquid fraction of the second refrigerant, is branched off, cooled and reduced in pressure in an expansion device and mixed with the condensed second refrigerant after the pressure of the latter has been reduced in an expansion device.

11. The method as claimed in claim 10, wherein said branched-off part of the gaseous fraction of the second refrigerant is cooled against a gaseous mixture of nitrogen and methane from a nitrogen stripper which is used to separate nitrogen from the liquefied natural gas.

12. The method as claimed in any one of claims 8—11, wherein the second refrigerant, after it has evaporated at least partly, is used for cooling in a heat-exchanger part of the second refrigerant after its pressure has been raised in a compressor installation.

13. A method of liquefying a natural gas as claimed in any one of the claims 1—12, substantially as described with particular reference to the drawing accompanying the provisional specification.

R. C. ROGERS,
Chartered Patent Agent,
Shell Centre,
London, SE1 7NA.
Agent for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1980
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

1572900 PROVISIONAL SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*